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Impact of the Middle Jurassic diversification of *Watznaueria* (coccolith-bearing algae) on the carbon cycle and δ^{13}C of bulk marine carbonates

Baptiste Suchéras-Marx [a,*], Abel Guihou [b], Fabienne Giraud [c], Christophe Lécuyer [a], Pascal Allemand [a], Bernard Pittet [a], Emanuela Mattioli [a]

[a] *UMR CNRS 5276 LGL-TPE, Université Claude Bernard Lyon 1, Ecole Normale Supérieure Lyon, Campus de la DOUA, Bâtiment Géode, 69622 Villeurbanne Cedex, France*
[b] *Lamont-Doherty Earth Observatory of Columbia University, 61 Route 9W, Palisades, NY 10964-8000, USA*
[c] *ISTerre, UMR 5275, Université de Grenoble 1, 1381 rue de la piscine, BP 53, 38041 Grenoble Cedex 9, France*

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ABSTRACT

During the Mid Mesozoic Revolution, thought to have started 200 Ma ago (Late Triassic), the production of calcium carbonate in the ocean shifted from platform and epicontinental seas to the open ocean, concurrently with the diversification of coccolithophorids. In this regard, the radiation of the coccolith genus *Watznaueria* during the Middle Jurassic is thought to represent one of the most important steps of this diversification. Nevertheless, the timing of this diversification remains poorly constrained, and its possible impact on global carbon budgets remains unclear. In this study, we present new records of nannofossil fluxes and carbon stable isotope composition from sedimentary deposits of Lower Bajocian age from the Cabo Mondego (Portugal) reference section to further address the possible impact of this diversification on the Middle Jurassic global carbon cycle. Our results show that calcareous nannofossil fluxes increase markedly from the upper part of the Aalenian to the Early Bajocian, coinciding with a 0.75‰ positive shift in carbon isotope compositions of bulk carbonate. Reconstructions of mass accumulation rates indicate that nannofossil fluxes increased by two orders of magnitude (from 10^9 to 10^{11} nannofossils/m^2/yr) during the corresponding time interval, mainly related to the rise of *Watznaueria* genus, whose relative abundance jumped from 2% to 20% of the total rock composition. The calculated amount of carbon derived from calcareous nannofossils deposited in the Early Bajocian seas was, however, 10 to 20 times lower than current levels. Mass balance calculations indicate that the increase of nannofossil flux throughout the studied interval was most likely not the main cause of the accompanying isotopic perturbation, suggesting a limited role of the Early Bajocian diversification on the global carbon cycle. Our results show that while the diversification of *Watznaueria* throughout the Bajocian caused a major increase in the flux of pelagic carbonate to the deep ocean, it was most likely quantitatively insufficient to have a large impact on the global biogeochemistry of the oceans.

1. Introduction

Pelagic carbonate production is the main output of the carbon cycle from the ocean to the Earth's crust (Sundquist and Visser, 2004) and has a significant impact on climate (e.g., Westbroek et al., 1993; Rost and Riebesell, 2004 and citations within). At present, calcium carbonate ($CaCO_3$) in the open ocean is mainly produced by coccolithophores and planktonic foraminifera. Consequently, the δ^{13}C and δ^{18}O values of deep-sea carbonates should reflect the composition of the communities of calcareous nannofossils and foraminifers (Bralower, 2002; Stoll and Ziveri, 2004).

The calcareous nannofossils are composed of coccolithophores and other micrometric calcifying *incertae sedis* (e.g., *Schizosphaerella*, *Nannoconus*,…). Coccolithophores, a type of golden-brown algae producing small carbonate platelets called coccoliths, appeared during the Late Triassic, 225 Ma ago (Bown, 2005) and dominated pelagic carbonate production until the rise of planktonic foraminifers at the end of the Early Cretaceous (~— 100 Ma) (Norris, 1991; Hay, 2004). Various studies have pointed out the key role of calcareous nannofossils upon the Jurassic carbon cycle (e.g., Bornemann et al., 2003; Hay, 2004; Erba, 2006; Goddéris et al., 2008; Mattioli et al., 2008, 2009). However, calcareous nannofossils may have been strictly restricted to shelves and shallow marine environments until the Late Jurassic and their abundance was too low to play the key role they are now playing in the modern global carbon cycle (Hay, 2004; Rost and Riebesell, 2004). The shift in carbonate production from shelves to open oceans by pelagic producers, termed the "Mid Mesozoic Revolution" (Ridgwell, 2005), is considered to be a tremendous event in ocean chemistry history, but its precise timing and impact on global carbon budgets remain unclear.

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* Corresponding author.
E-mail addresses: baptiste.sucheras@pepsmail.univ-lyon1.fr, baptiste.sucheras@gmail.com (B. Suchéras-Marx).

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In this context, the Early Bajocian (Middle Jurassic, ~170 Ma) constitutes a key time interval of the "Mid Mesozoic Revolution" in that it witnessed the diversification of the important coccolith genus *Watznaueria* (Mattioli and Erba, 1999; Erba, 2006; Tiraboschi and Erba, 2010). Indeed, this genus dominated the coccolith community for over 80 Myr, and its initial diversification could have therefore triggered the dominance of coccolithophores over the oceanic carbonate production. Interestingly, the diversification of *Watznaueria* appears to have been time coincident with a major carbon cycle perturbation, as suggested by the marked positive carbon isotope excursion recorded by oceanic carbonates in several European Lower Bajocian marine successions (Corbin, 1994; Bartolini et al., 1996, 1999; Hesselbo et al., 2003; O'Dogherty et al., 2006). Nevertheless, the cause of this excursion remains unclear. It might be linked to an increase in oceanic primary productivity. Furthermore, the change in calcareous nannofossil diversity and abundance are poorly quantified during this interval, hence precluding the reconstruction of potential cause–effect relationships between these events.

In this study, we present new measurements of bulk carbonate carbon isotope composition ($\delta^{13}C_{carb}$) and calcareous nannofossil absolute abundance from the Aalenian–Bajocian reference section at Cabo Mondego, Portugal, in order to address the potential links between diversification of calcareous nannofossil assemblages and carbon cycle dynamics during the Mid Jurassic. Using these records, we quantitatively investigate: (1) the contribution of nannofossil carbonate to the global oceanic carbon cycle, and (2) whether the diversification of *Watznaueria* by changing the bulk carbonate composition may have driven the Early Bajocian positive carbon isotope excursion.

2. Geological setting

The Cabo Mondego section is located in the Lusitanian basin, on the western Atlantic coast of Portugal near Figueira da Foz (Fig. 1). The succession is represented by marine deposits of Late Toarcian to Kimmeridgian age (Ruget-Perrot, 1961). Cabo Mondego is the Global Stratotype Section and Point (GSSP) for the Aalenian/Bajocian boundary (Pavia and Enay, 1997) as well as the Auxiliary Stratotype Section and Point (ASSP) for the Bajocian/Bathonian boundary (Fernandez-Lopez et al., 2009). Numerous ammonites, as well as other macro- or micro-paleontological remains such as belemnites, brachiopods, bivalves, ostracods, foraminifers, coccoliths, plant debris, and zoophycos trace fossils have been collected throughout the succession, allowing for the establishment of a precise biostratigraphical framework (Henriques et al., 1994).

The studied part of the Cabo Mondego section (Fig. 2) extends from the latest Aalenian (Concavum ammonite Zone) to the end of the Early Bajocian (base of the Humphriesianum ammonite Zone). The Early Bajocian is divided into four ammonite zones; Discites, Laeviuscula, Propinquans (equivalent of the Sauzei Zone of other regions), and Humphriesianum. The sedimentary succession consists of alternating marlstone and limestone (Fig. 2) and the carbonate fraction is exclusively micritic or microsparitic calcite (Henriques et al., 1994). The sediments corresponding to the Concavum (~5.5 m thick) and Discites (~7.2 m thick) zones are characterized by irregular nodular beds but fairly regular alternations of ~20 cm argillaceous limestone and marlstone beds. The interval corresponding to the base of the Laeviuscula (~36 m thick) Zone is limestone-dominated. At the base of the Propinquans (~32 m thick) Zone, the argillaceous limestones beds become more regular and thicker in comparison to the base of the section through the Humphriesianum (~7 m) Zone. From the Propinquans Zone, the succession becomes limestone-dominated.

3. Material and methods

3.1. $CaCO_3$ quantification and bulk carbonate stable isotope measurements

Calcium carbonate ($CaCO_3$) content was measured on forty-one samples. Approximately 300 mg of powdered bulk sediment was dissolved using 1 N HCl and the amount of CO_2 released from the sample was measured using a Dietrich-Frühling™ calcimeter. Carbon isotope composition of bulk samples was measured using an auto sampler Multiprep™ coupled to a GV Isoprime® mass spectrometer. For each sample, an aliquot of 350 to 500 μg was reacted with anhydrous over-saturated phosphoric acid at 90 °C for 20 min. Each sample has been duplicated two times. Isotopic compositions are quoted using delta notation in permil relative to VPDB. All sample measurements were duplicated and adjusted to the international reference NIST NBS19. Reproducibility is on average ~0.02‰ (2σ) for $\delta^{13}C_{carb}$ values.

3.2. Nannofossil quantification and flux estimation

The forty-one samples selected for nannofossil analysis were from the same intervals as those analyzed for isotopes. Calcareous nannofossil abundance and pelagic carbonate production were calculated following the method developed by Mattioli and Pittet (2002). Samples were prepared following the random settling method for absolute abundance quantification described by Beaufort (1991) and modified by Geisen et al. (1999). Using a Zeiss Axioskop 40 optical microscope with a magnification ×1000, at least 300 specimens per slide were counted. In seventeen slides, however, less than 300 specimens were counted, therefore counting was realized on at least one transverse corresponding to 150 fields of view. Three main nannofossil groups (*Schizosphaerella* spp., an *incertae sedis* frequently attributed to

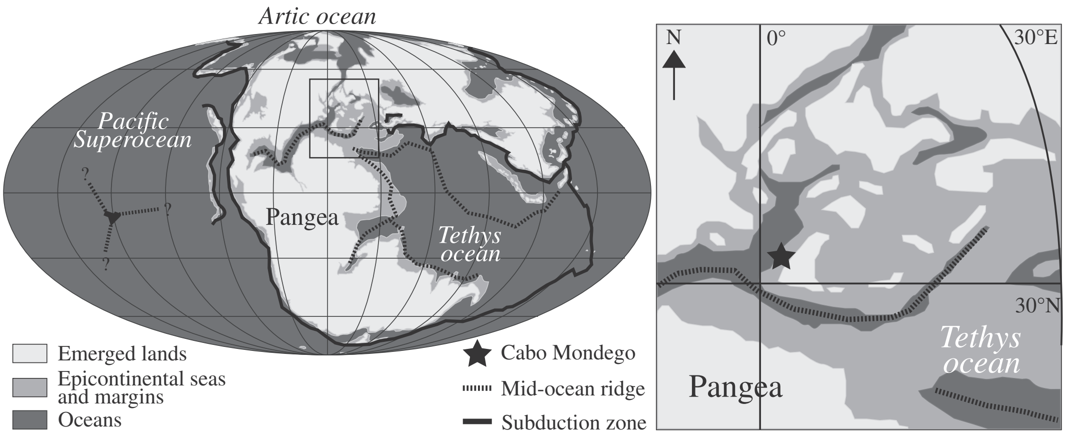

Fig. 1. Paleogeographic distribution of oceans and lands during the Middle Jurassic (after Blakey, 2005). On the left, a global view with subduction zones and mid-ocean ridges; and on the right, focus on the western Tethys with the localization of the Cabo Mondego section in the Lusitanian basin.